Structure of multi-component/multi-Yukawa mixtures

L. Blum†§ and M. Arias†

†Department of Physics, P.O. Box 23343, University of Puerto Rico, Rio Piedras, PR 00931-3343 and Department of Mathematics, Hill Center Rutgers University, Piscataway N.J. 08854

Abstract. Recent small angle scattering experiments reveal new peaks in the structure function $S(k)$ of colloidal systems (S.H. Chen et al [1]), in a region that was inaccessible with older instruments. It has been increasingly evident that a single (or double) Yukawa MSA-closures cannot account for these observations, and three or more terms are needed. On the other hand the MSA is not sufficiently accurate[2] more accurate theories such as the HNC have been tried. But while the MSA is asymptotically exact at high densities [3]it does not satisfy the low density asymptotics. This has been corrected in the soft-MSA [4, 5] by adding exponential type terms. The results compared to experiment and simulation for liquid sodium by Rahman and Paskin (as shown in [4]) are remarkably good. We use here a general closure of the Ornstein Zernike equation which is not necessarily the MSA closure [6].

$$c_{ij}(r) = \sum_{n=1}^{M} \mathcal{K}_{ij}^{(n)} e^{-z_n r}/r \qquad \mathcal{K}_{ij}^{(n)} = K^{(n)} \delta_i^{(n)} \delta_j^{(n)}; \qquad r \geq \sigma_{ij} \quad (1)$$

with the boundary condition for $g_{ij}(r) = 0$ for $r \leq \sigma_{ij}$. This general closure of the Ornstein Zernike equation will go well beyond the MSA since it has been tested by Monte Carlo simulation for tetrahedral water [7], toroidal ion channels [8] and polyelectrolytes [9]. For this closure we get for the Laplace transform of the pair correlation function an *explicitly* symmetric result

$$2\pi\tilde{g}_{ij}(s) = -\frac{e^{-s\sigma_{ij}}}{D_\tau(s)} \left\{ \frac{1}{s^2} + \frac{1}{s}Q'_{ij}(\sigma_{ij}) + \sum_{m=1}^{M} \frac{z_m \tilde{\mathcal{X}}_i^{(m)} f_j^{(m)}}{s+z_m} \right\}$$

$$(2)$$

This function is also easily transformed into $S(k)$ by replacing $s \Rightarrow ik$. For low density situations (dilute colloids) $D_\tau(s) \sim 1 + \mathcal{O}(\rho)$ and the $S(k)$ is a sum of M Lorentzians. For hard sphere PY mixtures we get the simple (compare [10, 11])

$$2\pi\tilde{g}_{ij}(s) = -\frac{e^{-s\sigma_{ij}}}{s^2 D_\tau(s)} \left\{ 1 + s\left[(Q^{HS})'_{ij}(\sigma_{ij}) \right] \right\}$$

where $D_\tau(s)$ is a scalar function. For polydisperse electrolytes in the MSA a simpler expression is also obtained (compare [12]) . An explicit continued fraction solution of the 1 component multiyukawa case is also given.

§ To whom correspondence should be addressed (lesblum@yahoo.com)

Submitted to: *J. Phys.: Condens. Matter*

1. Introduction

There are many problems of practical and academic interest that can be formulated as closures of some kind of either scalar or matrix Ornstein-Zernike (OZ) equation. These closures can always be expressed by a sum of exponentials, which do form a complete basis set if we allow for complex numbers [13, 14]. It is of practical interest to be able to relate small angle scattering experiments as directly as posible to theoretical (molecular) parameters. For a number of systems the MSA ([13, 15, 16])has been generally adequate ([1, 17]). The GOCM which is a the single peak-single Yukawa closure-MSA description is adequate in the simple cases. However, recent high resolution experiments have shown that to account for the additional peaks seen in the SANS experiments more yukawas are required [2, 18, 19]. The MSA and HNC closures of the OZ equation slightly underestimate the height of the interaction peak in the structure factor, whereas a close comparison of the cluster peak position is somewhat hindered by the limited resolution in Q of the simulation data, because the largest simulation box is never big enough. In most part of the practical range of potential parameters, the theoretical predictions coming from the two closures have comparable accuracy. Therefore, for fitting the neutron scattering intensity distributions, analytical structure factors are preferable since the resolution of the equations is more stable and fast.

Our present solution makes the direct comparison between theory and experiment feasible since a simple expression for the Fourier transform $S(Q)$ is proposed which is directly related to the closure of the OZ equation. In fact with the very mild assumption made is that the direct correlation function can be expanded as

$$c_{ij}(r) = \sum_{n=1}^{M} K_{ij}^{(n)} e^{-z_n(r-\sigma_{ij})}/r = \sum_{n=1}^{M} \mathcal{K}_{ij}^{(n)} e^{-z_n r}/r; \qquad r > \sigma_{ij} \qquad (3)$$

In the factorizable case (which is also the electrostatic charge case), we have

$$K_{ij}^{(n)} = K^{(n)} \delta_i^{(n)} \delta_j^{(n)}; \quad \mathcal{K}_{ij}^{(n)} = K^{(n)} d_i^{(n)} d_j^{(n)}; \quad \delta_i^{(n)} = d_i^{(n)} e^{-z_n \sigma_i/2} \qquad (4)$$

with

$$g_{ij}(r) = 0 \quad for \quad r \leq \sigma_{ij}.$$

Here z_n can be a complex number, and then eq.(3) is a complete function basis set. This closure works very well with a number of potentials, that include Lennard-Jones, Buckingham, and liquid metals [4, 20]. The effective interaction among charged colloids and globular proteins in solution is also well described by this potential which is the sum of a short range part attraction, usually accounting for van der Waals or entropic forces, plus a long range repulsion (of up to a few particle diameters), arising from screened electrostatic potential[21]. The two-Yukawa (2Y) fluid, consisting of particles interacting with this potential can be usefully applied to a wide variety of systems such as C60 fullerenes at high temperature[22], globular proteins[23, 24], and the Derjaguin-Landau- Verwey-Overbeek (DLVO)[25] potential for liophobic colloids.

While the initial motivation was to study simple approximations like the Mean Spherical (MSA) or Generalized Mean Spherical Approximation (GMSA), the availability of closed form solutions for the general closure of the hard core OZ equation makes it possible to write down analytical solutions for any given approximation that can be formulated by writing the direct correlation function $c(r)$ outside the hard core as

$$c(r) = \sum_{n=1}^{M} K^{(n)} e^{-z_n(r-\sigma)}/r = \sum_{n=1}^{M} \mathcal{K}^{(n)} e^{-z_n r}/r \tag{5}$$

In this equation $K^{(n)}$ is the interaction/closure constant used in the general solution first found by Blum and Hoye (which we will call BH78) [20], while $\mathcal{K}^{(n)}$ is the definition used in the later general solution by Blum, Vericat and Herrera (BVH92 in what follows) [26]. In this work we will use the more common notation of BVH92. The case of factored interactions was discussed by Blum, [27, 28] and by Ginoza [29, 30, 31, 32]. The general solution of this problem [26] is given in terms of the scaling matrix $\boldsymbol{\Gamma}$ which will comply with the physical constraints of the systems (Blum et al. [14, 33, 34]). The solution of the resulting algebraic equations has a number of branches (Pastore [35]). The rigorous analysis of this question is very complex. We have used the following working hypothesis:

(i) The singularities of the equations are poles, branch cuts and essential (exponential) sigularities.

(ii) The physical branch is the one for which the correct zero density result is obtained. This is equivalent to what is done in the rigorous treatment van der Waals theory, and includes metastable regions and spinodals.

(iii) The analysis of the repulsive part of the potential is more delicate since it is clearly related to the exponential singularities, and the convexity of the limiting high density configurations [36].

For only one component the matrix $\boldsymbol{\Gamma}$ can be assumed to be diagonal without loss of generality, and explicit expressions for the closure relations for any arbitrary number of Yukawa exponents M were obtained. The solution is then remarkably simple in the MSA since then explicit formulas for the thermodynamic properties are obtained. However there are undetermined integration constants in the entropy which have to be adjusted to get the correct limiting behavior [17].

2. Summary of Previous Work

We study the Ornstein-Zernike (OZ) equation

$$h_{ij}(12) = c_{ij}(12) + \sum_{k} \int d3 h_{ik}(13) \rho_k c_{kj}(32) \tag{6}$$

where $h_{ij}(12)$ is the molecular total correlation function and $c_{ij}(12)$ is the molecular direct correlation function, ρ_i is the number density of the molecules i, and $i = 1, 2$ is

the position $\vec{r}_i$, $r_{12} = |\vec{r}_1 - \vec{r}_2|$ and σ_{ij} is the distance of closest approach of two particles i, j. The direct correlation function is

$$c_{ij}(r) = \sum_{n=1}^{M} K_{ij}^{(n)} e^{-z_n(r-\sigma_{ij})}/r, \qquad r > \sigma_{ij} \tag{7}$$

and the pair correlation function is

$$h_{ij}(r) = g_{ij}(r) - 1 = -1, \qquad r \leq \sigma_{ij} \tag{8}$$

We use the Baxter-Wertheim (BW) factorization of the OZ equation

$$[\mathbf{I} + \rho\mathbf{H}(\mathbf{k})][\mathbf{I} - \rho\mathbf{C}(k)] = \mathbf{I} \tag{9}$$

where I is the identity matrix, and we have used the notation

$$\mathbf{H}(k) = 2\int_0^\infty dr \cos(kr)\mathbf{J}(r) \tag{10}$$

$$\mathbf{C}(k) = 2\int_0^\infty dr \cos(kr)\mathbf{S}(r) \tag{11}$$

The matrices J and S have matrix elements

$$J_{ij}(r) = 2\pi \int_r^\infty ds\, s h_{ij}(s) \tag{12}$$

$$S_{ij}(r) = 2\pi \int_r^\infty ds\, s c_{ij}(s) \tag{13}$$

$$[\mathbf{I} - \rho\mathbf{C}(k)] = [\mathbf{I} - \rho\mathbf{Q}(k)]\left[\mathbf{I} - \rho\mathbf{Q}^T(-k)\right] \tag{14}$$

where $\mathbf{Q}^T(-k)$ is the complex conjugate and transpose of $\mathbf{Q}(k)$. The first matrix is non–singular in the upper half complex k-plane, while the second is non–singular in the lower half complex k-plane.

It can be shown that the factored correlation functions must be of the form

$$\mathbf{Q}(k) = \mathbf{I} - \rho\int_{\lambda_{ji}}^\infty dr e^{ikr}\mathbf{Q}(r) \tag{15}$$

where we used the following definition

$$\lambda_{ji} = \frac{1}{2}(\sigma_j - \sigma_i) \tag{16}$$

$$\mathbf{S}(r) = \mathbf{Q}(r) - \int dr_1 \mathbf{Q}(r_1)\rho\mathbf{Q}^{\mathbf{T}}(r_1 - r) \tag{17}$$

Similarly, from Eq. (14) and Eq. (9) we get, using the analytical properties of Q and Cauchy's theorem

$$\mathbf{J}(r) = \mathbf{Q}(r) + \int dr_1 \mathbf{J}(r - r_1)\rho\mathbf{Q}(r_1) \tag{18}$$

The general solution is discussed in [27, 29, 34], and yields

$$q_{ij}(r) = q_{ij}^0(r) + \sum_{n=1}^{M} D_{ij}^{(n)} e^{-z_n r} \qquad \lambda_{ji} < r \tag{19}$$

$$q_{ij}^0(r) = (1/2)A_j[(r - \sigma_j/2)^2 - (\sigma_i/2)^2] + \beta_j[(r - \sigma_j/2) - (\sigma_i/2)]$$
$$+ \sum_{n=1}^{M} C_{ij}^{(n)} e^{-z_n \sigma_j/2}[e^{-z_n(r-\sigma_j/2)} - e^{-z_n \sigma_i/2}] \qquad \lambda_{ji} < r < \sigma_{ij} \tag{20}$$

The parameters $A_j, \beta_j, C_{ij}, D_{ij}$ are defined below and in Appendix 1.

3. The Laplace Transforms and the structure functions

From Eq. (18) we obtain the Laplace transform of the pair correlation function

$$2\pi \sum_{\ell} \tilde{g}_{i\ell}(s)[\delta_{\ell j} - \rho_{\ell}\tilde{q}_{\ell j}(is)] = \tilde{q}_{ij}^{0'}(is) \tag{21}$$

where

$$\tilde{q}_{ij}^{0'}(is) = \int_{\sigma_{ij}}^{\infty} dr e^{-sr}[q_{ij}^0(r)]'$$

$$= [(1 + s\sigma_i/2)A_j + s\beta_j]e^{-s\sigma_{ij}}/s^2 - \sum_m \frac{z_m}{s + z_m}e^{-(s+z_m)\sigma_{ij}}C_{ij}^{(m)} \tag{22}$$

and

$$e^{s\lambda_{ji}}\tilde{q}_{ij}(is) = \sigma_i^3\psi_1(s\sigma_i)A_j + \sigma_i^2\phi_1(s\sigma_i)\beta_j + \tag{23}$$

$$\sum_m \frac{1}{s + z_m}[(C_{ij}^{(m)} + D_{ij}^{(m)})e^{-z_m\lambda_{ji}} - C_{ij}^{(m)}e^{-z_m\sigma_{ji}} - z_m\sigma_i\phi_0(s\sigma_i)C_{ij}^{(m)}e^{-z_m\sigma_{ji}}]$$

where

$$\psi_1(x) = [1 - x/2 - (1 + x/2)e^{-x}]/(x^3) = \frac{\sigma^2}{2z}e^{-z\sigma/2}i_1(z\sigma/2)$$

$$i_1(x) = \frac{1}{x^2}(\sinh x - x\cosh x)$$

$$\phi_1(x) = [1 - x - e^{-x}]/(x^2) = x\psi_1(x) - \phi_0(x)/2; \qquad \phi_0(x) = \frac{[1 - e^{-x}]}{x} \tag{24}$$

In the factored case (see eq(4))

$$D_{ij}^{(m)} = -\delta_i^{(m)}a_j^{(m)}; \quad C_{ij}^{(m)} = \left(\delta_i^{(m)} - \frac{\mathcal{B}_i^{(m)}}{z_m}\right)a_j^{(m)}; \quad \mathcal{B}_i^{(m)} = 2\pi \sum_k \rho_k g_{ik}^{(m)}\delta_k^{(m)} \tag{25}$$

We remember that [26]

$$2\pi\sigma_{ij}g_{ij}(\sigma_{ij}) = q_{ij}'(\sigma_{ji}^-) - q_{ij}'(\sigma_{ji}^+)$$

$$= A_j(\sigma_i/2) + \beta_j - \sum_{m=1}^M \left(z_m\delta_i^{(m)} - \mathcal{B}_i^{(m)}\right)a_j^{(m)}e^{-z_m\sigma_{ij}} \tag{26}$$

and

$$\tilde{q}_{ij}(is) = e^{-s\lambda_{ji}}\sigma_i^3\psi_1(s\sigma_i)A_j + e^{-s\lambda_{ji}}\sigma_i^2\phi_1(s\sigma_i)\beta_j -$$

$$\sum_m \frac{e^{-z_m\lambda_{ji}}}{s + z_m} \left(\delta_i^{(m)} + (\hat{\mathcal{B}}_i^{(m)} - \delta_i^{(m)})\left\{1 - e^{-(z_m+s)\sigma_i}[1 + z_m\sigma_i\phi_0(\sigma_i s)]\right\}\right)a_j^{(m)} \tag{27}$$

which can be written in the form

$$\mathbf{M}_{ij}(s) = \delta_{ij} - \rho_i q_{ij}(is)$$
$$= \delta_{ij} - a_i b_j - c_i d_j - \sum_m^M e_i^{(m)} f_j^{(m)} \equiv \sum_{\alpha=1}^{M+2} a_i^{(\alpha)} b_j^{(\alpha)} \tag{28}$$

with

$$a_i = \rho_i \sigma_i^3 \psi_1(s\sigma_i) e^{s\sigma_i/2} \qquad b_j = A_j e^{-s\sigma_j/2} = A_j^0 e^{-s\sigma_j/2} + \frac{\pi}{\Delta} \sum_n a_j^{(n)} P^{(n)} e^{-s\sigma_j/2}$$

$$c_i = \rho_i \sigma_i^2 \phi_1(s\sigma_i) e^{s\sigma_i/2} \qquad d_j = \beta_j e^{-s\sigma_j/2} = \beta_j^0 e^{-s\sigma_j/2} + \frac{2\pi}{\Delta} \sum_n a_j^{(n)} \Delta^{(n)} e^{-s\sigma_j/2}$$

$$e_i^{(m)} = \rho_i e^{s\sigma_i/2} \sigma_i^2 \varphi_1^{(m)}(s\sigma_i) \qquad f_j^{(m)} = a_j^{(m)} e^{z_m \sigma_j/2}$$

$$\varphi_1^{(m)}(s\sigma_i) = \frac{e^{z_m \sigma_i/2}}{s + z_m} \left\{ \frac{\mathcal{B}_i^{(m)}}{z_m} - e^{-z_m \sigma_i} \left(\frac{\mathcal{B}_i^{(m)}}{z_m} - \delta_i^{(m)} \right) \left[1 + \frac{z_m}{s}(1 - e^{-s\sigma_i}) \right] \right\} \tag{29}$$

Notice that eq.(22) can be written as

$$\tilde{q}_{ik}^{0'}(is) = -\tilde{a}_i b_k - \tilde{c}_i d_k - \sum_m^M \tilde{e}_i^{(m)} f_k^{(m)} \equiv \tilde{\mu}_{ij} = \sum_{\alpha=1}^{M+2} \tilde{a}_i^{(\alpha)} b_j^{(\alpha)} \tag{30}$$

with

$$\tilde{\mathbf{a}}_i = \frac{(1 + s\sigma_i/2)}{s^2} e^{-\frac{s\sigma_i}{2}}$$

$$\tilde{\mathbf{c}}_i = \frac{e^{-\frac{s\sigma_i}{2}}}{s}$$

$$\tilde{\mathbf{e}}_i^{(m)} = e^{-\frac{s\sigma_i}{2}} \frac{z_m}{s + z_m} \mathcal{X}_i^{(m)}; \quad \mathcal{X}_i^{(m)} \equiv e^{-z_m \sigma_i} \left(\frac{\mathcal{B}_i^{(m)}}{z_m} - \delta_i^{(m)} \right) \tag{31}$$

With this notation we can rewrite eq.(21) as

$$2\pi \tilde{g}_{ij}(s) = \sum_k \tilde{\mu}_{ik} \left[\mathcal{M}_{ij}(s) \right]^{-1} \tag{32}$$

After some algebra we get the general and simple result

$$2\pi \tilde{g}_{ij}(s) = -\frac{\tilde{\mu}_{ij}(s)}{D_\tau(s)} \tag{33}$$

with

$$D_\tau = Det \left| \delta_{\alpha,\beta} - \left(\sum_i a_i^{(\alpha)} b_i^{(\beta)} \right) \right|; \tag{34}$$

4. Selected applications

We now apply the general result eq.(33) to a few selected examples of interest:

4.1. The Polydisperse hard spheres mixture

For hard spheres

$$A_j = \frac{2\pi}{\Delta}\left[1 + \frac{\pi\zeta_2}{2\Delta}\sigma_j\right] = \frac{2\pi}{\Delta}\left[1 + \frac{\zeta_2}{2}\beta_j\right]$$

$$\beta_j = \frac{\pi}{\Delta}\sigma_j$$

Then we get, using the definitions of eq.(28-31)

$$a_i = \rho_i\sigma_i^3\psi_1(s\sigma_i) \qquad b_j = A_j^0$$
$$c_i = \rho_i\sigma_i^2\phi_1(s\sigma_i) \qquad d_j = \beta_j^0$$

$$(35)$$

and also

$$\tilde{\mathbf{a}}_i = (1 + s\sigma_i/2)e^{-s\sigma_i}/s^2$$
$$\tilde{\mathbf{c}}_i = e^{-s\sigma_i}/s$$

$$(36)$$

The pair correlation function is

$$2\pi\tilde{g}_{ij}(s) = -\frac{e^{-s\sigma_{ij}}}{s^2 D_\tau}\left\{1 + s\left[(Q^{HS})'_{ij}(\sigma_{ij})\right]\right\}$$

$$D_\tau = 1 - \sum_j \rho_j\sigma_j^2\left\{\sigma_j\psi_1(s\sigma_j)A_j^0 - \phi_1(s\sigma_j)\beta_j^0 + \frac{4\pi^2}{\Delta^2}\sum_i \rho_i\sigma_i^3\psi_1(s\sigma_i)\phi_1(s\sigma_j)\lambda_{ji}\right\}$$

$$(37)$$

4.2. The electrolyte limit

We take the limit [27]

$$z_m = 0 \tag{38}$$

of the general definitions. Then,

$$a_i = \rho_i\sigma_i^3\psi_1(s\sigma_i) \qquad b_j = A_j^0 + \frac{\pi}{\Delta}a_j^0 P_n = A_j$$
$$c_i = \rho_i\sigma_i^2\phi_1(s\sigma_i) \qquad d_j = \beta_j^0 + a_j^0\Delta_N = \beta_j$$
$$e_i^{(0)} = \rho_i e^{s\sigma_i/2}\sigma_i^2\varphi_1^{(0)}(s\sigma_i) \qquad f_j^{(0)} = a_j^{(0)}e^{-s\sigma_j/2}$$
$$\varphi_1^{(0)}(s\sigma_i) = \frac{1}{s}\left\{\frac{\pi}{\Delta}P_n\phi_1(s\sigma_i) - X_i^{(0)}[1 + \phi_0(s\sigma_i)]\right\}$$

$$(39)$$

Moreover

$$\tilde{q}_{ij}^{0'}(is) = [(1 + s\sigma_i/2)A_j + s\beta_j]e^{-s\sigma_{ij}}/s^2 - \sum_m \frac{z_m}{s + z_m}e^{-(s+z_m)\sigma_{ij}}C_{ij}^{(m)}$$

$$= \frac{e^{-s\sigma_{ij}}}{s^2}\left\{[(1 + s\sigma_i/2)A_j + s\beta_j] + s\mathcal{B}_i^{(0)}a_j^{(0)}\right\}$$

$$= \frac{e^{-s\sigma_{ij}}}{s^2}\left\{[(1 + s\sigma_i/2)A_j^0 + s\beta_j^0] + s\mathcal{X}_i^{(0)}a_j^{(0)}\right\}$$

(40)

and also

$$\tilde{\mathbf{a}}_i = \frac{(1 + s\sigma_i/2)}{s^2}e^{-\frac{s\sigma_i}{2}}$$

$$\tilde{\mathbf{c}}_i = \frac{e^{-\frac{s\sigma_i}{2}}}{s}$$

$$\tilde{\mathbf{e}}_i^{(0)} = \frac{z_m}{s + z_m}e^{-(s)\sigma_i/2}e^{-z_m\sigma_i}(\hat{\mathcal{B}}_i^{(m)} - \delta_i^{(m)}) \Rightarrow \frac{1}{s}e^{-s\sigma_i/2}\mathcal{B}_i^{(0)}$$

(41)

so that from eq.(33) we get the symmetric expression (compare [20])

$$2\pi\tilde{g}_{ij}(s) = -\frac{\tilde{\mu}_{ij}}{D_\tau}$$

$$= -\frac{e^{-s\sigma_{ij}}}{s^2 D_\pm}\left\{1 + s\left[\frac{\sigma_i}{2}A_j^0 + \beta_j^0 + \mathcal{X}_i^{(0)}a_j^{(0)}\right]\right\}$$

(42)

with

$$D_\pm = Det\begin{vmatrix} 1 - (ab) & -(ad) & -(af) \\ -(cb) & 1 - (cd) & -(cf) \\ -(eb) & -(ed) & 1 - (ef) \end{vmatrix}$$

(43)

where the scalar products (see also [20]) are defined by

$$(ab) = \sum_i a_i b_i, \quad (cd) = \sum_i c_i d_i, \quad (ef) = \sum_i e_i f_i \quad ....$$

(44)

and we use the definitions of eq.(39).

5. THE PRIMARY CLOSURE

The MSA closure condition obtained from Eq.(7) is

$$2\pi K\delta_i^{(n)}\delta_j^{(n)}/z_n = \sum_\ell D_{i\ell}^{(n)}[\delta_{\ell j} - \rho_\ell \tilde{q}_{j\ell}(iz_n)]$$

(45)

Using the results of the last section we got [34]

$$2\pi K \delta_j^{(n)} + z_n \sum_\ell \mathcal{I}_{j\ell}^{(n)} a_\ell^{(n)}$$

$$- \sum_m \frac{z_n}{z_n + z_m} \{\sum_k \rho_k a_k^{(n)} a_k^{(m)}\} \left[\sum_\ell \mathcal{J}_{j\ell}^{(n)} [\Pi_\ell^{(m)} - z_m X_\ell^{(m)}] - \mathcal{I}_{j\ell}^{(n)} X_\ell^{(m)} \right] = 0 \tag{46}$$

6. The 1 Component Case: An explicit continued fraction solution

In the one component case eq.(46) is simply [34]

$$- 2\pi K_n \rho \, [X_n]^2 = z_n \beta_n \left[1 + \sum_m \frac{1}{z_n + z_m} \beta_m \right] \tag{47}$$

with

$$X_n = \frac{\delta_n}{\mathcal{I}^{(n)} + \Gamma_n \mathcal{J}^{(n)}} \tag{48}$$

$$\beta_n = \rho a_n X_n \tag{49}$$

In the diagonal approximation we get explicit equations for the scaling parameters β_i [14] (See appendix III.,[14]) We recall that

$$\mathcal{J}^{(n)} = \sigma \phi_0(z_n \sigma) + \rho \Delta^{J,(n)} \tag{50}$$

$$\Delta^{J,(n)} = -\frac{2\pi}{\Delta} \sigma^4 \psi_1(z_n \sigma) \tag{51}$$

and

$$\mathcal{I}^{(n)} = 1 + \rho \Delta^{I,(n)} \tag{52}$$

$$\Delta^{I,(n)} = \sigma^2 \phi_0(z_n \sigma) \frac{\pi}{2\Delta} \sigma - \frac{2\pi}{\Delta} \sigma^3 \psi_1(z_n \sigma) \left[1 + \left(\zeta_2 \frac{\pi}{2\Delta} \right) \sigma + \sigma z_n/2 \right] \tag{53}$$

and we have used the definition (76).

The solution of the β equations is obtained solving the linear equation [14]

$$\overrightarrow{\beta} = \left[\hat{\mathcal{M}} \right]^{-1} \cdot 2 \overrightarrow{\Gamma}$$

$$\tag{54}$$

where

$$\hat{\mathcal{M}} = \begin{bmatrix} 1 & 1 - \gamma_{12} & 1 - \gamma_{13} & \cdot \\ 1 + \gamma_{12} & 1 & 1 - \gamma_{23} & \cdot \\ 1 + \gamma_{13} & 1 + \gamma_{23} & 1 & \cdot \\ \cdot & \cdot & \cdot & \cdot \end{bmatrix} ; \qquad \overrightarrow{\beta} = \begin{bmatrix} \beta_1 \\ \beta_2 \\ \cdot \end{bmatrix} ; \qquad \overrightarrow{\Gamma} = \begin{bmatrix} \Gamma_1 \\ \Gamma_2 \\ \cdot \end{bmatrix} \tag{55}$$

and

$$\gamma_{nm} = \frac{2\Gamma_n + z_n - 2\Gamma_m - z_m}{z_m + z_n} \tag{56}$$

We give the soultions for the first few cases [14]:

(i) 1 Yukawa $\beta_1 = 2\Gamma_1$

(ii) 2 Yukawas

$$\beta_1 = \frac{2\Gamma_2 - \beta_s}{\gamma_{12}} \qquad \beta_2 = \frac{-2\Gamma_1 + \beta_s}{\gamma_{12}} \qquad \beta_s = \frac{2\Gamma_2 - 2\Gamma_1}{\gamma_{12}} \tag{57}$$

(iii) 3 Yukawas: This case is slightly more complicated:
The resolvent is

$$\overrightarrow{\mu}^{(3;1)} = \begin{pmatrix} \gamma_{23} \\ \gamma_{31} \\ \gamma_{12} \end{pmatrix}, \tag{58}$$

so that the explicit solution is

$$\beta_1 = \left[\frac{1}{d_3}\right]\left[\gamma_{23}\left(\frac{2\overrightarrow{\Gamma} \cdot \overrightarrow{\mu}^{(3;1)}}{d_3} + s_{23}\right) - z_{23}\right]$$

$$\beta_2 = -\left[\frac{1}{d_3}\right]\left[\gamma_{13}\left(\frac{2\overrightarrow{\Gamma} \cdot \overrightarrow{\mu}^{(3;1)}}{d_3} + s_{13}\right) - z_{13}\right]$$

$$\beta_3 = \left[\frac{1}{d_3}\right]\left[\gamma_{12}\left(\frac{2\overrightarrow{\Gamma} \cdot \overrightarrow{\mu}^{(3;1)}}{d_3} + s_{12}\right) - z_{12}\right] \tag{59}$$

where $d_3 = \gamma_{12} + \gamma_{23} - \gamma_{13}$.

$$\beta_s = \frac{2\overrightarrow{\Gamma} \cdot \overrightarrow{\mu}^{(3;1)}}{d_3} \tag{60}$$

The general case of $n \geq 3$ can be found in the work of Blum et al. [14, 38]

6.1. The 1 Yukawa case

In the 1-Yukawa, 1 component case [27] the closure equation is simply

$$-2\pi\rho K_1[X_1]^2 = z_1\beta_1\left[1 + \frac{\beta_1}{2z_1}\right]; \tag{61}$$

so that putting it all together we get the equation

$$y_1 = 2\Gamma_1(\Gamma_1 + z_1)\left[\mathcal{I}^{(1)} + \Gamma_1\mathcal{J}^{(1)}\right]^2; \qquad y_1 = -\frac{2\pi\rho K_1\delta_1^2}{z_1} \tag{62}$$

The physical branch yields the recursion relation

$$\Gamma_1^{(1)} = \frac{y_1}{2z_1\left[\mathcal{I}^{(1)}\right]^2}; \qquad \Gamma_1^{(n+1)} = \frac{y_1}{2(\Gamma_1^{(n)} + z_1)\left[\mathcal{I}^{(1)} + \Gamma_1^{(n)}\mathcal{J}^{(1)}\right]^2} \tag{63}$$

For large $z_1 \geq 3$, we may disregard the exponential terms in Eqs(76), and then we get the simple

$$\mathcal{I}^{(1)} = 1 + \frac{2\pi\rho\left(1 + \frac{\pi\rho}{3} - \frac{\pi z_1\rho}{4}\right)}{z_1^3\Delta^2}; \qquad \mathcal{J}^{(1)} = \frac{1}{z_1} + \frac{\pi\rho(-2+z_1)}{z_1^3\Delta} \qquad (64)$$

from where

$$\Gamma_1 = \frac{y_1}{2z_1\left(1 - \frac{\pi^2\rho^2}{2z_1^2\Delta^2} + \frac{2\pi\rho(3+\pi\rho)}{3z_1^3\Delta^2}\right)^2}; \qquad \Gamma_2 = \frac{y_1}{2(\Gamma_1+z_1)\mathcal{D}_{\Gamma,1}^2} \qquad (65)$$

with

$$\mathcal{D}_{\Gamma,1} = 1 + \frac{1}{z_1^2\Delta}\left[\frac{-(\pi^2\rho^2)}{2\Delta} + \frac{2\pi\rho\left(1+\frac{\pi\rho}{3}\right)}{z_1\Delta} - \frac{2y_1\left(-\Delta + \frac{2\pi\rho(2-z_1)}{z_1^2}\right)}{\left(2 - \frac{\pi^2\rho^2}{z_1^2\Delta^2} + \frac{4\pi\rho\left(1+\frac{\pi\rho}{3}\right)}{z_1^3\Delta^2}\right)^2}\right]$$

The solution is always convergent for the atractive case, and we do get the Onsagerian limits for large densities and zero temperature correctly. It has been successfully tested numerically against other numerical methods [37] and Hernando, (unpublished, but using Pastore's criterion). For the repulsive case $K > 0$ this equation has poles and unphysical divergencies occurring when the Onsagerian limits are attained. These divergencies are removed when a suitable reference hard core is introduced.

6.2. The multiyukawa case

The above solution is valid for any number of Yukawas $n \geq 1$. We write Eq. (47) in matrix form:

$$\begin{bmatrix} y_1 \\ y_2 \\ . \end{bmatrix} = \begin{bmatrix} 1 + \beta_1/s_{11} & \beta_1/s_{12} & . \\ \beta_2/s_{12} & 1 + \beta_2/s_{22} & . \\ . & . & . \end{bmatrix}\begin{bmatrix} \beta_1 \\ \beta_2 \\ . \end{bmatrix} \qquad (66)$$

Using equations (54) and (55) we find

$$\vec{\Gamma} = \frac{1}{2}\hat{\mathcal{M}}\cdot\begin{bmatrix} 1 + \beta_1/s_{11} & \beta_1/s_{12} & . \\ \beta_2/s_{12} & 1 + \beta_2/s_{22} & . \\ . & . & . \end{bmatrix}^{-1}\cdot\begin{bmatrix} y_1/[\mathcal{I}^{(1)} + \Gamma_1\mathcal{J}^{(1)}]^2 \\ y_2/[\mathcal{I}^{(2)} + \Gamma_2\mathcal{J}^{(2)}]^2 \\ . \end{bmatrix} \qquad (67)$$

with

$$s_{nm} = z_n + z_m$$

This relation is the extension of Eq.(63) to the multiyukawa case: The iteration follows exactly the same steps, only that now we have to use the extra equation (54): The first iterate is

$$\vec{\Gamma}^{(0)} = \frac{1}{2}\begin{bmatrix} 1 & 1 - \frac{z_{12}}{s_{12}} & 1 - \frac{z_{13}}{s_{13}} & . \\ 1 + \frac{z_{12}}{s_{12}} & 1 & 1 - \frac{z_{23}}{s_{23}} & . \\ 1 + \frac{z_{13}}{s_{13}} & 1 + \frac{z_{23}}{s_{23}} & 1 & . \\ . & . & . & . \end{bmatrix}\cdot\begin{bmatrix} y_1/[\mathcal{I}^{(1)}]^2 \\ y_2/[\mathcal{I}^{(2)}]^2 \\ . \end{bmatrix}; \quad z_{nm} = z_n - z_m$$

$$(68)$$

and then

$$\overrightarrow{\Gamma}^{(n+1)} = \frac{1}{2}\hat{\mathcal{M}}^{(n)} \cdot \left[\left\{ \begin{array}{ccc} 1 + \beta_1/s_{11} & \beta_1/s_{12} & . \\ \beta_2/s_{12} & 1 + \beta_2/s_{22} & . \\ & . & . & . \end{array} \right\}^{(n)} \right]^{-1} \cdot \left[\begin{array}{c} y_1/[\mathcal{I}^{(1)} + \Gamma_1^{(n)}\mathcal{J}^{(1)}]^2 \\ y_2/[\mathcal{I}^{(2)} + \Gamma_2^{(n)}\mathcal{J}^{(2)}]^2 \\ . \end{array} \right] \quad (69)$$

where the superscript (n) indicates the level of the iteration.

7. Summary of results

- A new formulation of the pair distribution function for a large class of systems represented by a multiyukawa closure of the Ornstein-Zernike equation (1) which includes systems such as water, ionic mixtures, ion channels and polymers is presented. This formulation is considerably simpler and more explicit than those in the literature because it involves directly measurable parameters such as the contact pair distribution function. It is also capable of handling the new improved versions of the MSA and the realistic octupolar model of water [7].

- The new result shown in equation (2) is simple and explicit: For example in the case of the SANS and SAXS experiments [1, 2] our result show explicitly the connection between the number of peaks in the diffraction spectra to the theoretical formula. because we get for dilute systems a sum of M Lorentzians, one for each yukawa term in the closure.

- The one component case has been discussed in several papers, largely in collaboration with J. Hernando [6], although most of the numerical results are still unpublished. The conclusion is that once the branch points are identified the continued fraction formalism *always* converges (see also[37]).

8. Appendix I: The algebraic solution of the general Yukawa closure of the Ornstein Zernike equation

We quote the results from the review of Blum and Hernando [34]: The solution of the system of equations (19,20) yields

$$A_j = A_j^0 + \frac{\pi}{\Delta}\sum_n a_j^{(n)} P^{(n)}; \qquad \beta_j = \beta_j^0 + \frac{2\pi}{\Delta}\sum_n a_j^{(n)}\Delta^{(n)} \qquad (70)$$

where

$$A_j^0 = \frac{2\pi}{\Delta}\left[1 + (1/2)\zeta_2\frac{\pi}{\Delta}\sigma_j\right]; \qquad \beta_j^0 = \frac{\pi}{\Delta}\sigma_j \qquad (71)$$

$$\frac{\pi}{\Delta}P^{(n)} = \frac{1}{z_n}\sum_\ell \rho_\ell\left[A_\ell^0 X_\ell^{(n)} + 2\beta_\ell^0(z_n X_\ell^{(n)} - \Pi_\ell^{(n)})\right] \qquad (72)$$

$$\Delta^{(n)} = -\frac{1}{z_n^2}\sum_\ell \rho_\ell\left[X_\ell^{(n)}(A_\ell^0 - z_n\beta_\ell^0) + 2\beta_\ell^0(z_n X_\ell^{(n)} - \Pi_\ell^{(n)})\right] \qquad (73)$$

We have

$$\Pi_j^{(n)} = \hat{B}_j^{(n)} + \Delta^{(n)} + \frac{\pi}{2\Delta}\sigma_j P^{(n)};$$
$$X_i^{(n)} = \delta_i^{(n)} + \sigma_i \hat{B}_i^{(n)}\phi_0(z_n\sigma_i) + \sigma_i\Delta^{(n)} \tag{74}$$

$$\Pi_j^{(n)} = \hat{\xi}_j^{(n)} + \sum_\ell \hat{\mathcal{I}}_{j\ell}^{(n)}\hat{B}_\ell^{(n)}$$
$$X_j^{(n)} = \gamma_j^{(n)} + \sum_\ell \hat{\mathcal{J}}_{j\ell}^{(n)}\hat{B}_\ell^{(n)} \tag{75}$$

where

$$\hat{\mathcal{I}}_{j\ell}^{(n)} = \delta_{j\ell} - \rho_\ell\sigma_\ell^2[\beta_j^0\phi_1(z_n\sigma_\ell) + A_j^0\sigma_\ell\psi_1(z_n\sigma_\ell)]$$
$$\hat{\mathcal{J}}_{j\ell}^{(n)} = \delta_{j\ell}\sigma_j\phi_0(z_n\sigma_\ell) - 2\rho_\ell\beta_j^0\sigma_\ell^3\psi_1(z_n\sigma_\ell) \tag{76}$$

with

$$\hat{\xi}_j^{(n)} = -\frac{1}{z_n^2}\sum_\ell \rho_\ell\delta_\ell^{(n)}[A_j^0 + z_n Q'(\sigma_{\ell j})]$$
$$\hat{\gamma}_j^{(n)} = \delta_j^{(n)} - \frac{2\pi\sigma_j}{z_n^2\Delta}\sum_\ell \rho_\ell\delta_\ell^{(n)}\left(1 + \frac{z_n\sigma_\ell}{2}\right) \tag{77}$$

Here we define [34]:

$$\zeta_n = \sum_k \rho_k\sigma_k^n \tag{78}$$

$$\Delta = 1 - \pi\zeta_3/6 \tag{79}$$

$$\tilde{g}_{ij}(s) = \int_0^\infty dr r g_{ij}(r)e^{-sr} \tag{80}$$

$$\gamma_{ij}^{(n)} = 2\pi\tilde{g}_{ij}(z_n)\rho_j/z_n \tag{81}$$

$$\hat{B}_j^{(n)} = \sum_i z_n\delta_i^{(n)}\gamma_{ji}^{(n)}e^{z_n\sigma_{ij}} \tag{82}$$

$$\psi_1(s\sigma_i) = \frac{1}{2}[\gamma_z(3, s\sigma_i) - \gamma_z(2, s\sigma_i)]$$
$$\phi_1(s\sigma_i) = [\gamma_z(2, s\sigma_i) - \gamma_z(1, s\sigma_i)] \tag{83}$$

with the incomplete γ function

$$\gamma_z(n, z) = \frac{(n-1)!}{z^n}\left[1 - e^{-z}\sum_i^{n-1}\frac{z^i}{i!}\right] \tag{84}$$

9. Appendix II: Inverse of $\mathbf{M}_{ij}(s)$

$$\widehat{\mathbf{M}}_{ij}(s) = \delta_{ij} - \mu_{ij}; \qquad \mu_{ij} = \sum_{\alpha=1}^{\alpha_m} a_i^{(\alpha)} b_j^{(\alpha)}$$

(85)

The determinant of this matrix can be expanded in its minors $\mathcal{M}_{ij}$

$$D_T = Det|\delta_{ij} - \mu_{ij}| = \sum_i [\delta_{ij} - \mu_{ij}] (-)^{i+j} \mathcal{M}_{ij} \quad ; \qquad \forall j$$

(86)

This determinant can also be condensed into a simpler and more compact form

$$D_T = D_\tau = \left| \delta_{\alpha,\beta} - \left(\sum_i a_i^{(\alpha)} b_i^{(\beta)} \right) \right|$$

(87)

which can also be expanded in its minors $\mathbf{M}^{(\alpha,\beta)}$

$$D_\tau = \sum_\beta \left(\delta_{\alpha,\beta} - a^{(\alpha)} \bullet b^{(\beta)} \right) [-]^{\alpha+\beta} \mathbf{M}^{(\alpha,\beta)}; \quad \forall \alpha$$
$$= \sum_\beta \left(\delta_{\alpha,\beta} - a^{(\alpha)} \bullet b^{(\beta)} \right) \mathcal{A}^{(\alpha,\beta)}; \quad \mathcal{A}^{(\alpha,\beta)} = [-]^{\alpha+\beta} \mathbf{M}^{(\alpha,\beta)}$$

(88)

Using Cramer's rule then we find the general inverse

$$[\mathbf{M}^{-1}(s)]_{ij} = \delta_{ij} + \frac{1}{D_\tau} \sum_\beta a_i^{(\alpha)} b_j^{(\beta)} \left\{ \mathcal{A}^{(\alpha,\beta)} \right\}; \quad \forall \{\alpha, \beta\}$$

(89)

$$\sum_k \{\delta_{ik} - \mu_{ik}\}.[\mathbf{M}^{-1}(s)]_{kj} = \delta_{ij}$$
$$\sum_k \{\delta_{ik} - \mu_{ik}\}.[\delta_{ij} + \frac{1}{D_\tau} \sum_\beta (-)^{\alpha+\beta} a_k^{(\alpha)} b_j^{(\beta)} \left\{ \mathcal{M}^{(\alpha,\beta)} \right\}] = \delta_{ij}$$
$$\sum_k \left[\sum_\gamma a_i^{(\gamma)} b_k^{(\gamma)} \right] . \left[\frac{1}{D_\tau} \sum_\beta a_k^{(\alpha)} b_j^{(\beta)} \left\{ \mathcal{A}^{(\alpha,\beta)} \right\} \right] = \mu_{ij}$$

(90)

which means that we must satisfy

$$\mu_{ij} = \sum_{\gamma,\beta} a_i^{(\gamma)} b_j^{(\gamma)} \left[\frac{1}{D_\tau} \sum_k b_k^{(\gamma)} a_k^{(\alpha)} \right] \mathcal{A}^{(\alpha,\beta)}$$

(91)

$$\sum_k \left(\mu_{ik} [\mathbf{M}^{-1}(s)]_{ij}^{\alpha,\beta} \right) = \sum_\alpha a_i^{(\alpha)} \sum_k b_k^{(\beta)} \left(-\frac{1}{D_\tau} \sum_\gamma a_k^{(\gamma)} b_j^{(\delta)} \left\{ \mathcal{A}_{\gamma,\delta} \right\} \right); \qquad \forall \delta$$
$$= \frac{1}{D_\tau} \sum_\beta (-)^{\alpha+\beta} a_i^{(\alpha)} b_j^{(\beta)} \left\{ \mathcal{M}^{(\alpha,\beta)} \right\}] + \sum_\alpha a_i^{(\alpha)} \left(-\frac{1}{D_\tau} \sum_\gamma \left[\sum_k b_k^{(\beta)} a_k^{(\gamma)} \right] \left\{ \mathcal{A}_{\gamma,\delta} \right\} \right) b_j^{(\delta)};$$
$$= \mu_{ij}$$

(92)

as it should

10. Acknowledgements

We wish Prof. Sow Hsin Chen a very happy and healthy 70th birthday. The subject of this paper was inspired in conversationss with him.

[1] Liu, Y. Chen, W.-R. and Chen, S.H.,2005, *J. Chem. Phys.***122** , 044507.

[2] Broccio, M ., Costa, D. Liu, Y. and Chen, S.H., Preprint (2005).

[3] Rosenfeld, Y. and Blum, L., 1986, *J. Chem. Phys.* , **85** 1556.

[4] Blum, L. and Narten, A.H., 1972, *J. Chem. Phys.*, **56** , 5197.

[5] Narten, A.H., Blum L., and Fowler, R. H., 1974, *J. Chem. Phys.*, **60** 3378.

[6] Blum, L. and Hernando, J. A., 2001,*Condensed Matter Theories*,**16**,411, S. Hernandez and J. W. Clark, editors, Nova Publishers New York.

[7] Blum, L., Vericat F. and Degreve L. , *Physica A* **265** , 396.

[8] Enriquez, A. and Blum, L., 2005, *Mol. Phys.* , **103** 3201.

[9] Blum, L., and Bernard, O., 2004, *Proc. International School of Physics "Enrico Fermi", Course CLV,* Mallamace, F. and Stanley, H. E., Editors, IOS Press, Amsterdam, **155**, 335.

[10] Lebowitz, J.L., 1964, *Phys. Revs* , 1964, **133**, A895.

[11] Blum, L. and Stell, G., 1979, *J. Chem. Phys.***71** 42.

[12] Blum, L. and Hoye, J. S.,1977, *J. Phys. Chem.*, **81** ,1311.

[13] Blum, L. and Herrera J.N., 1999 *Mol. Phys.* **96**, 821.

[14] Blum, L. and Ubriaco, M., 2000, *Mol. Phys.*, **98**, 829.

[15] Percus J.K. and Yevick G.,1964, *Phys. Revs.* ,**110** 250 .

[16] Lebowitz, J.L. , and Percus, J.K., 1966, *Phys. Revs*,**144**, 251.

[17] Lin, Y.Z. Li, Y.G. Lu Y. F., and Liu, Z. P. 2002, *J. Chem. Phys.***117** 10165.

[18] Wu, C. F. and Chen, S.H., 1987, *J. Chem. Phys.*, **87**, 6199.

[19] Wu, C. F. and Chen, S.H., 1988, *Biopolymers*, **27**, 1065.

[20] Blum L. and Høye J.S., 1978, *J. Stat. Phys.*,**19** , 317.

[21] Morales, V. Anta, J.A. and Lago, S. 2003, *Langmuir* ,**19**, 475 .

[22] Kaldasch, J., Laven J., and Stein, H. N. 1996, *Langmuir* ,**12**, 6197.

[23] Victor, J.M. and Hansen, J.P.,1985,*J. Chem. Soc., Faraday Trans.***2-81**, 43 .

[24] Grimson, M. J., J. Chem. Soc.,1982,*J. Faraday Trans.* **2 79**, 817.

[25] Verwey, E. J. W. and Overbeek, J. TH. G. , 1948, *Theory of the Stability of Lyophobic Colloids* , Elsevier, Amsterdam.

[26] Blum L., Vericat F. and Herrera , J.N.,1992, *J. Stat. Phys.*,**66**, 249.

[27] Blum L. , 1980, *J. Stat. Phys.*,**22** ,661.

[28] Blum L., 1975, *Mol. Phys.***30**, 1529 .

[29] Ginoza M., 1986, *J.Phys. Soc. Japan*,**55**, 95 .

[30] Ginoza M., 1986, *J.Phys. Soc. Japan* ,**55**, 1782.

[31] Ginoza M., 1990, *Mol. Phys.*,**71**, 145.

[32] Ginoza M. and Yasutomi M.,1998, *J. Stat. Phys.*,**90**, 1475 .

[33] Blum L. and Herrera J.N.,1998 *Mol. Phys.* , **95**, 425.

[34] Blum L. and Hernando, J. A., 2002, *J. of Phys.: Cond. Matt.* **14** 10933 .

[35] Pastore, G. , 1988, *Mol. Phys.* , **63**, 731.

[36] Hernando, J. A., and Blum L., 1993, *J. of Phys.: Cond. Matt.*, **5** Suppl. 33A, A109.

[37] Vazquez, O. R., Herrera , J.N. and Blum, L., 2003, *Physica A*, **325** 319 .

[38] Blum, L. and Ubriaco, M.,2000, *Physica A*, **279** 224.